Surface and electronic structure of diamond nanoparticles

T. van Buuren, T. Willey, C. Bostedt, R. Muelenburg, J.Y. Raty, G. Galli, L. Terminello
Chemistry and Material Science Department, Lawrence Livermore National Laboratory

Nanometer sized diamond is a constituent of diverse systems ranging from interstellar dusts and meteorites to carbonaceous residues of detonations. We have conducted a number of experiments tightly coupled to theory that demonstrates the impact of surfaces on the electronic and atomic structure of diamond nanoparticles produced via a detonation synthesis method. The nanodiamond K-edge absorption and emission spectra for 3-4 nm clusters show the same features as the bulk material and no blue shift is observed, contrary to previous experiments on nanocrystalline diamond films.[1] Therefore the 3nm nano-sized diamonds do not display the characteristic property of other group IV nanoparticles: a strong widening of the energy gap between the conduction and valence bands owing to quantum-confinement effects. Standard density-functional calculations on clusters in which the diamond surface bonds are terminated with hydrogen atoms, show that the bandgap begins to increase above the bulk value only for clusters smaller than 1 nm. Ab-initio calculations were preformed to investigate the effect of surface relaxation on diamond nanoparticles as well. To represent a true surface, pairs of hydrogens were removed whose interatomic distances were within 5% of the H_2 bond length and the surface atoms were allowed to relax. In this study, the surfaces spontaneously reconstructed into a fullerene-like surface but this reconstruction induced only small changes in the calculated gap values. [2] Clear signatures of these surface reconstructions were identified as pre-edge features in measured C 1s absorption spectra. The C1s core exciton feature clearly observed in the K-edge absorption edge of bulk diamond is shifted and broadening due to increased overlap of the excited electron with the core hole in the small particle. Also the depth of the second gap in the nanodiamond spectra is shallower than that of bulk diamond.

One of the weaknesses of the x-ray absorption measurement is that many particles are probed to produce the measured spectra. This is not a problem if one has a distribution of identical particles. However, with a finite size distribution or other inhomogeneity in the nanoparticle ensemble, the measured spectrum represents a combination of the spectra from all particles. To resolve and explore the electronic structure of individual quantum dots, we have employed the high spatial resolution possible from transmission electron microscopy and the electronic structure information possible with electron energy loss spectroscopy (TEM/EELS). The high spatial resolution of the TEM/EELS will allow us to; 1) make measurements of the electronic structure of the individual nanoparticles and 2) probe separately the surface and bulk structure of the nanoparticle. The TEM/EELS measurements on the diamond nanoparticles indicate that the core of the particle has similar electronic structure as bulk diamond, whereas the surface region looks much different. The EELS spectra of the surface region cannot be described by the EELS spectra from graphite or C-60 but seems to be a combination of both in agreement with our previous x-ray absorption and emission results.

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1 Y. K. Chang et al., Phys. Rev. Lett. **82**, 5377 (1999).
2 J.Y. Raty, G. Galli, C. Bostedt, T. Van Buuren, L.J. Terminello, Phys. Rev. Lett. Vol. **90**, p401 (2003).